| Sample Type                                                                                                                                                                                                                                              | Objective                                                                                                                                                              | Frequency of Analysis                                                                                                                                                                                  | Recommended<br>Control Limits                        | Recommended Corrective Action                                                                                                                                                                                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| External Calibration                                                                                                                                                                                                                                     |                                                                                                                                                                        | -                                                                                                                                                                                                      |                                                      |                                                                                                                                                                                                                                            |
| Calibration Standards (3-5 standards over the expected range of sample target analyte conc., with the lowest conc. Std at or near the MDL).                                                                                                              | Full calibration: Establish relationship<br>between instrument response and<br>target analyte conc.                                                                    | Follow manufacturer's or procedures in<br>specific analytical protocols. A min. 3<br>point calib.: Each set up, major<br>disruption, and when routine calib check<br>exceeds specific control limits.  | Linear regression, r>0.995.                          | Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.                                                                                                            |
| Calibration Verification                                                                                                                                                                                                                                 |                                                                                                                                                                        |                                                                                                                                                                                                        |                                                      |                                                                                                                                                                                                                                            |
| Calibration Check Standards (minimum of one mid-<br>range standard prepared independently from initial<br>calibration standards: an instrument internal standard<br>must be added to each calib. check std. when internal<br>std. calib. is being used). | Verify calibration.                                                                                                                                                    | After initial calibration or recalibration.<br>Every 10 samples,                                                                                                                                       | Mercury %R = 80-120%, all other metals %R = 90-110%. | Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.                                                                                                            |
| Method Detection Limit Determination                                                                                                                                                                                                                     |                                                                                                                                                                        |                                                                                                                                                                                                        |                                                      |                                                                                                                                                                                                                                            |
| Spiked matrix samples (analyte-free water samples to<br>which known amounts of target analytes have been<br>added; one spike for each target analyte at 3-10 times<br>the estimated MDL).                                                                | Establish or confirm MDL for analyte of interest.                                                                                                                      | Seven replicate analyses prior to use of method. Reevaluation of MDL annually.                                                                                                                         | Determined by program manager.                       | Redetermine MDL.                                                                                                                                                                                                                           |
| Accuracy and Precision Assessment                                                                                                                                                                                                                        |                                                                                                                                                                        |                                                                                                                                                                                                        |                                                      |                                                                                                                                                                                                                                            |
| Reference materials (SRMs or CRMs, covering the range of expected target analyte conc.).                                                                                                                                                                 | Assess method performance (initial method validation and routine accuracy assessment).                                                                                 | Method validation: As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment: one (preferably blind) per 20 samples or one batch. |                                                      | If matrix spikes are in control then proceed.<br>If not, determine cause and take appropriate<br>corrective action. Recalibrate and reanalyze<br>all suspect samples or flag all suspect data.                                             |
| Matrix spikes (field water samples to which known amounts of target analytes have been added: at least 5 times the concentration of the analyte of interest or 10 times the MDL).                                                                        | Assess matrix effects and accuracy (%Recovery) routinely.                                                                                                              | One per 20 samples or one per batch, whichever is more frequent.                                                                                                                                       | %R = 75-125%                                         | If SRMs are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data. |
| Matrix spike replicates (replicate aliquots of matrix spike samples; at least 5 times the concentration of the analyte of interest or 10 times the MDL).                                                                                                 | Assess method precision routinely.                                                                                                                                     | One duplicate per 20 samples or one per batch, whichever is more frequent.                                                                                                                             | RPD <25% for duplicates.                             | Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.                                                                                                            |
| Laboratory Duplicate                                                                                                                                                                                                                                     | Assess method precision                                                                                                                                                | One per 20 samples or one per batch, whichever is more frequent.                                                                                                                                       | RPD <25% for duplicates.                             | Determine cause, take appropriate corrective action. Recalibrate & reanalyze all suspect samples or flag all suspect data.                                                                                                                 |
| Field Replicate (replicate aliquots of water field samples).                                                                                                                                                                                             | Assess method precision routinely.<br>Assess total variability (i.e., population<br>variability, field or sampling variability,<br>and analytical method variability.) | 5% annual rate (5% of total number of<br>field samples per analytical procedure<br>per year, rounded up to nearest whole<br>number).                                                                   | RPD <25% for duplicates.                             | Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.                                                                                                            |

|                                                                                                                                                         |                                                 |                                                                                                                                                                                                                                                                                                 | Recommended                                                                                                                                                                                                                                                                                                      | Recommended Corrective                                                                                                                                                                                                                           |
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| Sample Type                                                                                                                                             | Objective                                       | Frequency of Analysis                                                                                                                                                                                                                                                                           | Control Limits                                                                                                                                                                                                                                                                                                   | Action                                                                                                                                                                                                                                           |
| Contamination Assessment                                                                                                                                |                                                 |                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                  |
| Laboratory Blanks (method, processing, bottle, filters, reagent).                                                                                       | reagents, etc.                                  | One method blank per 20 samples or one per batch, whichever is more frequent. At least one bottle blank per batch. One reagent blank prior to use of a new batch of reagent and whenever method blank exceeds control limits. One filter blank per new lot.                                     | Blanks <mdl analytes.<="" for="" target="" td=""><td>Determine cause of problem (e.g., contaminated reagents, equipment), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data.</td></mdl>                                                                                | Determine cause of problem (e.g., contaminated reagents, equipment), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data.                                                                                |
| Field Blanks, Travel Blanks, Equipment Blanks.                                                                                                          | from air, from surrounding environment, etc.    | One field equipment blank is required per 20 (or less) field water samples collected for trace metals analysis, including mercury. Pre-cleaned C-flex tubing used for each site w/peristaltic pump for depth-integration; or pre-cleaned syringe and pencil filter used at each site otherwise. | Blanks <mdl analytes.<="" for="" target="" td=""><td>Determine cause of problem (e.g., contaminated preservatives, equipment contamination, improper cleaning, exposure to airborne contaminants, etc.), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data.</td></mdl> | Determine cause of problem (e.g., contaminated preservatives, equipment contamination, improper cleaning, exposure to airborne contaminants, etc.), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data. |
| External QA Assessment                                                                                                                                  |                                                 |                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                  |
| Accuracy-based performance evaluation samples submitted to new laboratories by SWAMP QA Program.                                                        | 1                                               | Once prior to routine analysis of field samples.                                                                                                                                                                                                                                                | Determined by study manager.                                                                                                                                                                                                                                                                                     | Determine cause of problem and reanalyze sample. Do not begin analysis of field samples until laboratory initial capability is clearly demonstrated.                                                                                             |
| Mandatory interlaboratory exercises overseen by 3rd<br>party external ("referee") SWAMP QA Program officials<br>for all SWAMP participant laboratories. | Ongoing demonstration of laboratory capability. | One exercise per year.                                                                                                                                                                                                                                                                          | Determined by study manager.                                                                                                                                                                                                                                                                                     | Determine cause of problem and reanalyze sample. Further corrective action to be determined by QA manager.                                                                                                                                       |
| Voluntary, but encouraged, participation in NOAA-NIST intercalibration studies and CA-ELAP annual performance evaluations, as appropriate.              | Ongoing demonstration of laboratory capability. | One exercise per year.                                                                                                                                                                                                                                                                          | Determined by study manager.                                                                                                                                                                                                                                                                                     | Determine cause of problem and reanalyze sample. Further corrective action to be determined by QA manager.                                                                                                                                       |